



# FeOOH catalytic ozonation of oxalic acid and the effect of phosphate binding on its catalytic activity

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## ABSTRACT

The catalytic activity of FeOOH on ozonation of oxalic acid at pH 4.0 and 7.0 conditions was investigated in a semi-continuous experimental mode. The results indicate that FeOOH can effectively promote the generation of hydroxyl radicals ( $\cdot\text{OH}$ ) under acidic and neutral pH conditions, resulting in the enhancement of the degradation efficiency of oxalic acid by ozone. It is deduced that the hydroxyl groups both of in neutral state ( $\text{Me-OH}$ ) and positive charge state ( $\text{Me-OH}_2^+$ ) can perform as the active sites for ozone decomposition into hydroxyl radicals generation. The ligand exchange of hydroxyl groups by phosphate adsorption deteriorates the catalytic activity of FeOOH on ozonation, but the phosphate is found to desorb from FeOOH during the catalytic ozonation process, resulting in the reactivation of the catalytic activity of FeOOH.

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## 1. Introduction

The increasing organic pollution in water sources in last decades promoted the development of water treatment technologies. Ozonation has received much attention for its high oxidation potential on organic matters in water. While, ozone reacts slowly with some organic compounds and can not achieve complete mineralization. The deep catalytic ozonation of organic pollutants into carbon dioxide and water has been identified as one of the most efficient ways to destroy the refractory organic matters in water. According to the state of the catalysts, the catalytic ozonation is classified as homogeneous catalytic ozonation, in which ozone is activated by soluble metal ions such as  $\text{Fe(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Cd(II)}$ ,  $\text{Ag(I)}$ ,  $\text{Cr(III)}$  [1,2] and heterogeneous catalytic ozonation with the solid metal (hydr)oxides (e.g.  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeOOH}$ ) or metals/metal (hydr)oxides on supports ( $\text{Cu-Al}_2\text{O}_3$ ,  $\text{Cu-TiO}_2$ ,  $\text{Ru-CeO}_2$ ,  $\text{V-O/TiO}_2$ ,  $\text{V-O/silica}$  gel,  $\text{Co/Al}_2\text{O}_3$ , and  $\text{TiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ , etc.) and some porous

materials (for example, activated carbon and microporous and mesoporous silicate) as catalysts [1,3–9]. To avoid the separating difficulty of the soluble metal ions catalysts from aqueous solution, heterogeneous catalytic ozonation has been paid more attention in latest years, which has been proved to be effective for the removal of the resistant organic compounds from water [1,3–9].

Till now, research works on heterogeneous catalytic ozonation are mainly performed with pure water as background for catalyst activity evaluation and the reaction mechanism investigation. Although the organic matters are the target substances, the inorganic matters coexisting in the real water background may bring uncertain effect on the catalytic activity of the solid catalyst. In  $\text{CuO/Al}_2\text{O}_3$  catalytic ozonation process, the conversion of oxalic acid into  $\text{CO}_2$  was found to be restrained in the presence of phosphate ions [10]. Phosphate were reported to inhibit the catalytic activity of  $\alpha\text{-FeOOH}$  more significantly than and sulfate on ozonation of nitrobenzene, and the inhibition on the catalyst increased with the increasing concentration of sulfate or phosphate [9]. In the phosphate-buffered solution, the mineralization efficiency of oxalic acid, acetic acid and the succinic acid by  $\text{Al}_2\text{O}_3$  catalytic ozonation all lowered compared with that of in non-buffered solution [11].

For the metal (hydr)oxides type of catalysts, they are also the effective adsorbents for the inorganic ions in water [12–16]. It has to be highlighted that the great adsorption ability of inorganic ions

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constituents on metal (hydr)oxides may be the key reason that cause the decrease of their catalytic activity. The adsorption property of metal (hydr)oxide is of great importance for its catalytic activity of heterogeneous surface. Adsorption is often one of the stages of heterogeneous catalytic ozonation. There are generally three possible mechanisms of catalytic ozonation in heterogeneous systems which all relate with adsorption [1]: (1) chemisorption of ozone on the catalyst surface leading to the formation of active species which react with non-chemisorbed organic molecule; (2) chemisorption of organic molecule (associative or dissociative) on the catalytic surface and its further reaction with aqueous ozone; (3) chemisorption of both ozone and organic molecules and the subsequent interaction between chemisorbed species. Provided the active surface sites for target organics adsorption or ozone adsorption and decomposition are occupied by the inorganic ions in water, it may induce the blockage of the active surface sites for catalytic process, and even deactivate the catalysts permanently. Thus, the effect of inorganic ions adsorption on the catalytic activity of metal (hydr)oxide has to be taken into consideration when evaluating its real application potential. However, the fate of the catalytic activity of metal (hydr)oxide catalyst binding with the inorganic ions is still unclear and needs further investigation.

Taking FeOOH catalytic ozonation as the model heterogeneous catalytic ozonation system, oxalic acid and phosphate as the model organic compound and inorganic ion, the catalytic activity, catalyzing mechanism and the effect of inorganic ions adsorption on the catalytic activity of FeOOH catalyst are investigated in this study. FeOOH has been revealed to be the effective catalyst to assist ozone to degradation the resistant organic matters in water [9,17,18], and it is also the efficient adsorbent for the inorganic ions in water [13,14,19,20]. Oxalic acid is chosen as the model organic matter for the following reasons: (1) it is the degradation intermediate of several organic matters of ozonation process and is refractory to ozone molecule oxidation [21]; (2) it exists in the ionic forms in weak acidic and neutral pH conditions and should be adsorbed on FeOOH. And the reason that phosphate was selected as the model inorganic ions is owing to its strong affinity on FeOOH [14,19].

## 2. Experimental

### 2.1. Materials and reagents

Goethite (FeOOH) was prepared based on the methods described by Hiemstra et al. [22]. Freshly prepared 0.5 M  $\text{Fe}(\text{NO}_3)_3$  was slowly titrated with 2.5 M NaOH to pH 12. The suspension was aged at 60 °C for 72 h. The resulting suspension was dialyzed with Milli-Q water to remove the excess electrolytes until the electrical conductivity (EC) and the pH of the filtrate were remained constant. After dialysis, the suspension was placed in an evaporating dish and oven-dried for 6 h at 100 °C. The dry solid was weighted into weight needed, then bottled into polyethylene tubes and fully redispersed in Milli-Q water by ultrasonication for 24 h for further use. The prepared solid was confirmed to be goethite using X-ray diffraction (XRD) analysis (D/max 2550 X-ray Diffractometer, Rigaku, Japan). The BET surface area measured with  $\text{N}_2$  is 51.6 m<sup>2</sup>/g (Tristar3000 Surface area and porosity Analyzer, Micromeritics, USA). The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of the goethite was determined to be 7.2 by performing acid-base titrations of the suspended goethite in three different concentrations of  $\text{NaNO}_3$  [23]. Alkalimetric and acidimetric titration described by Stumm and Morgan [24] was carried out under high purity of nitrogen to determine the intrinsic values of the surface acidity constants. The intrinsic acidity constants of goethite are  $\text{pK}_{\text{int}}^1$  5.6 and  $\text{pK}_{\text{int}}^2$  8.7.

All chemicals used are analytical reagent grade and contain negligible phosphate impurity. They were used as received except 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 97%) was purified with powdered activated carbon under  $\text{N}_2$  atmosphere. Solutions were prepared with water purified by a Millipore Milli-Q UV Plus system. Sulfuric acid and sodium hydroxide were used for pH adjustment.

### 2.2. Ozonation procedure

Ozone oxidation experiments were carried out in semi-continuous mode. The cylindrical reactor was made of glass with inside diameter of 50 mm, a length of 700 mm. It was enclosed with tinfoil paper to avoid light-decomposition effect. Ozone was generated by a corona discharge ozone generator using air as feed gas (DHX-I, Harbin Jiujiu Electrochemistry Technology Co., Ltd., China). The ozone gas concentration was 0.45 mg/min with the constant flow rate of 400 ml/min at 293 K. Ozone was introduced into the reactor through a porous titanium plate laid at 50 mm height above the bottom. The offgas was adsorbed by the potassium iodide solution. Before the experimental operation, the oxalic acid solution and the goethite suspension were first added into the reactor, and then ozone was continuously fed into the reactor. Water samples were withdrawn at specific intervals. Sodium thiosulfate was used to quench further oxidation. The samples were filtered with 0.20  $\mu\text{m}$  syringe filter for quantification. Unless otherwise stated, the initial concentration of oxalic acid was 10  $\mu\text{M}$ . The pH of the reaction solution was not buffered in all the tests. After each run, the reactor was rinsed with 0.01 M of sulfuric acid and Milli-Q water repeatedly.

Ozone decomposition experiment was conducted in batch mode as follows: firstly, ozone was continuously fed into 300 ml Milli-Q water for 30 min, and then goethite suspension was added and the reaction bottle was sealed rapidly. At the same time the magnetic stirrer was switched on and the samples were withdrawn at intervals to determine the residual ozone concentration.

### 2.3. Adsorption experiments

#### 2.3.1. Phosphate adsorption experiments

Phosphate solutions with initial concentrations ranging from 3 to 300  $\mu\text{mol/l}$  were prepared using  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , which would result in both low and high phosphate loadings on goethite. Phosphate adsorption isotherms were determined in polyethylene bottles under a constant ionic strength of 0.01 M  $\text{NaNO}_3$  at  $25.00 \pm 1.00$  °C. After being shaken for 48 h, which has been established as adequate to reach equilibrium by our experiments on adsorption kinetics (data not shown), the samples were immediately filtered with a 0.20  $\mu\text{m}$  syringe filter. The filtrate was used to measure the aqueous phosphate concentration. The phosphate surface coverage was determined by calculating the difference between the initial phosphate concentration and the final phosphate concentration in the mixture suspension. The experiments were performed in duplicate to check the reproducibility of the results.

#### 2.3.2. Oxalic acid adsorption experiments

All oxalic acid adsorption experiments were carried out in ozonation reactor with air but not ozone bubbling into the reactor.

### 2.4. Analytical method

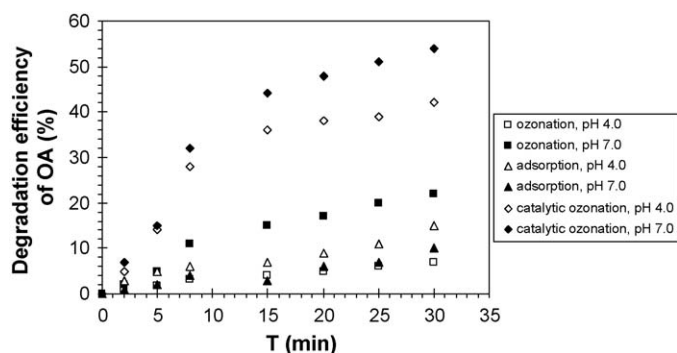
The oxalic acid, phosphate or sulfate were analyzed using an ion chromatograph (ICS 1000, Dionex) that was equipped with a 25  $\mu\text{l}$  loop injector, an electrochemical detector, an IonPac AS11-HC column (4 mm  $\times$  250 mm), and an online eluent generator. It was operated isocratically at 1 ml/min using 15 mM KOH solution as a

mobile phase. The data processing was performed using Chromeleon software (from Dionex). The mineralization degree of organics was measured by a Shimadzu TOC 3201 analyzer. Ozone concentration in aqueous solution was measured by indigo method [25]. The sample was determined immediately after sampling to avoid the unreacted potassium indigo trisulfonate being adsorbed on catalyst (0.75%, 1.72% and 2.87% of potassium indigo trisulfonate were found to be adsorbed on FeOOH in 2.5 min, 5 min and 10 min). A test without ozone presence was performed as control test. Electron spin resonance (ESR) trapping method was used to detect hydroxyl radicals. The samples for ESR analysis was prepared as follows: firstly, preparing the aqueous ozone stock by continuously purging ozone into Milli-Q water at 277 K, then adding the ozone stock solution into FeOOH suspension and reaction for a few minutes, and then sampling the ozonated solution to mix with phosphate-buffered DMPO solution quickly. Finally, syringing the mixture into a capillary tube and placing in the cavity of magnet for hydroxyl radicals determination. ESR spectra were recorded at room temperature with a Bruker EMX-8/2.7 spectrometer (ER 4119HS cavity). Instrument parameters were controlled as follows: microwave frequency, 9.875 GHz, microwave power, 20.0 mW, modulation frequency, 0.1 GHz, and modulation amplitude, 1 Gs. The pH was recorded with an Orion glass pH electrode and an Ag/AgCl double-junction reference electrode using a Metrohm pH meter. Commercial buffer solutions from Shanghai at pH 4.01 and 7.00 were used to calibrate the pH meter before pH measurement.

### 3. Results and discussion

#### 3.1. Degradation efficiency of oxalic acid by FeOOH catalytic ozonation

As pH values influence not only the decomposition of ozone in aqueous solutions, but also the surface properties of FeOOH and the dissociation of organic molecules in water, the experiments were performed at weak acid (pH 4.0) and neutral pH conditions (pH 7.0), respectively. The test at basic pH condition is not discussed here because of the strong self-decomposition of ozone under basic pH condition and the weak phosphate adsorption on FeOOH. The degradation efficiency of FeOOH catalytic ozonation on oxalic acid corresponding to reaction time is shown in Fig. 1. For comparative purpose, both oxalic acid adsorption on FeOOH and ozonation experiment in the absence of FeOOH were performed in the same system under identical experimental conditions. It is obvious from Fig. 1 that the presence of FeOOH remarkably enhanced the degradation efficiency of oxalic acid. At pH 4.0 and 7.0, the catalytic ozonation systems achieved 42% and 54% of degradation efficiencies, while only 7% and 22% of oxalic acid were



**Fig. 1.** Oxalic acid degradation by ozonation alone, FeOOH adsorption and FeOOH catalytic ozonation. *Experimental conditions:* ozone gas flow rate: 400 mL/min; ozone gas concentration: 0.45 mg/min; initial concentration of oxalic acid: 0.01 mM; FeOOH dose: 2 g/L;  $T = 293$  K.

degraded in the case of ozonation alone. Fifteen and ten percent of oxalic acid were adsorbed on FeOOH at pH 4.0 and 7.0, respectively. Besides, the TOC concentrations determined experimentally (omitted here) were found to be in agreement with that calculated from the residual concentration of the oxalic acid, which indicates the oxidation of oxalic acid leads to complete mineralization. The thoroughly mineralization of oxalic acid has also been reported in activated carbon heterogeneous catalytic ozonation system [6,26]. Comparing FeOOH catalytic ozonation with the cumulative effectiveness of ozonation alone and adsorption of oxalate ions on FeOOH, an augment of approximately 20% and 22% of oxalate ions degradation was observed at pH 4.0 and 7.0. Obviously, the presence of FeOOH has a synergistic effect with ozone on oxalic acid degradation.

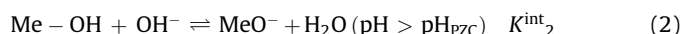
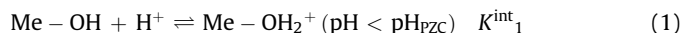
#### 3.2. Discussion on reaction mechanism of FeOOH catalytic ozonation

##### 3.2.1. Ozonation alone system

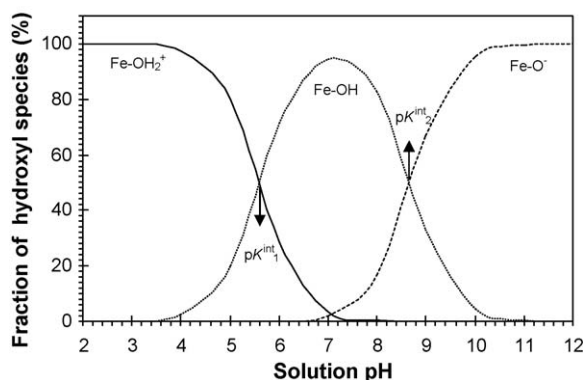
In aqueous solution, it is well known that ozone reacts with organic or inorganic compounds following two pathways, the direct selective reaction through ozone molecule and the nonselective reaction via hydroxyl radicals generated from ozone decomposition [1,27]. Under the tested pH conditions, oxalic acid exists in the form of oxalate ions ( $pK_{a1} = 1.25$ ;  $pK_{a2} = 3.81$ ; [28]). Hoigné and Bader investigated the ozonation of oxalic acid at pHs ranging from 2 to 8 and concluded that the direct reaction of ozone with oxalate ions can be considered negligible ( $k_{O_3} = 0.04 \text{ M}^{-1} \text{ s}^{-1}$ ; [21]). While, oxalate ions are prone to be oxidized by hydroxyl radicals with the reaction rate constant of  $7.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  [29]. Ozone molecule is the predominately oxidative species at acidic pH condition, while, the hydroxyl radicals reaction mechanism is followed at basic pH condition in ozonation system because the hydroxyl ions can initiate ozone decomposition to produce hydroxyl radicals [30]. In ozonation alone, the 22% of oxalate ions degradation efficiency at pH 7.0 should be due to the attack of hydroxyl radicals, which were produced via the ozone decomposition initiated by hydroxyl ions. Fewer yields of hydroxyl radicals should be responsible for only 7% of degradation efficiency at pH 4.0.

##### 3.2.2. Adsorption and FeOOH heterogeneous catalytic ozonation system

For heterogeneous catalytic ozonation system, the notable degradation efficiency for oxalate ions should depend on the surface properties of FeOOH. The presence of hydroxyl groups on the surface of metal (hydr)oxide are deemed as the most important chemical property, which influences organic compound adsorption and ozone decomposition on the surface of catalyst [1]. The acid/base properties of the surface hydroxyl groups can be changed with the conversion of  $pH_{PZC}$  and pH (as shown in Eqs. (1) and (2)). When the solution pH is near the  $pH_{PZC}$ , most of surface hydroxyls exist in neutral state. Otherwise, the oxide surface becomes protonated or deprotonated when solution pH is below or above its  $pH_{PZC}$ . With the intrinsic acidity constants, the fractions of various surface hydroxyl species of metal (hydr)oxide in water could be calculated as a function of pH [24]. Fig. 2 shows the variation of surface hydroxyl species of FeOOH corresponding to solution pH. At pH 4.0, the total protonation takes place and almost all the hydroxyl groups existed in the form of  $-\text{OH}_2^+$ , and the neutral hydroxyl group ( $-\text{OH}$ ) is the predominant species with the fraction of 94.4% at pH 7.0.



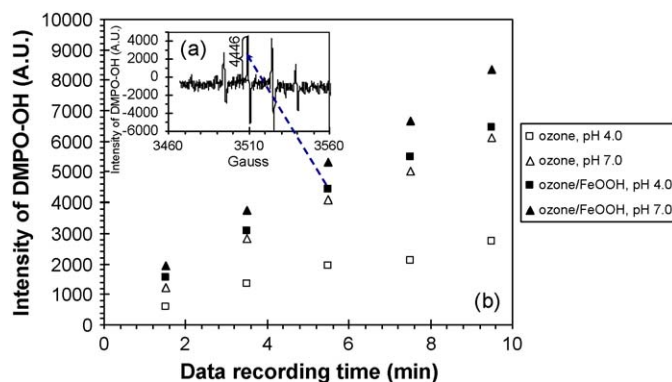
where  $K^{\text{int}}_1$  and  $K^{\text{int}}_2$  are the intrinsic ionisation constants.



**Fig. 2.** Distribution of different surface hydroxyl species on FeOOH as a function of pH.

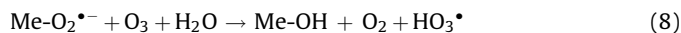
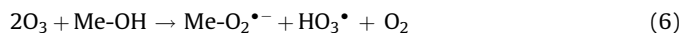
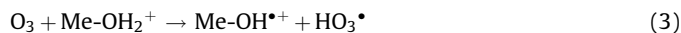
The charge of the surface hydroxyl group will influence ionized organic compound adsorption. As shown in Fig. 2, the concentration of the surface site  $\text{-OH}_2^+$  that can support the adsorption of oxalate anions decreased with the increase of pH, thus resulted in the higher adsorption efficiency of oxalate ions at pH 4.0 compared with that at pH 7.0 (Fig. 1). In previous studies, adsorption of organic compounds on metal (hydr)oxides catalyst was found to play a key role for heterogeneous catalytic ozonation process. When studying the catalytic activity of  $\text{TiO}_2/\text{Al}_2\text{O}_3$  to improve the ozonation of oxalic acid in water, it was proposed that it is the adsorbed oxalic acid reacts directly with ozone in solution, and the oxalic acid adsorption stage is the rate-limiting step [31]. In  $\text{MnOx}/\text{GAC}$  catalytic ozonation adsorption of nitrobenzene on catalyst is an important step, which has a direct influence on the catalytic effectiveness of the heterogeneous catalytic system [32]. Adsorption also did part contribution for oxalate removal in FeOOH catalytic ozonation (Fig. 1); however, the relatively low adsorption efficiency of oxalate ions on FeOOH compared with the catalytic degradation efficiency indicates that adsorption of oxalate ions is not the critical reason for the catalytic activity of FeOOH on ozonation of oxalic acid.

In the presence of metal (hydr)oxides catalyst, the elevated oxidizing capacity is often ascribed to the promotion of hydroxyl radicals generation. A series of experiments were carried out to determine the formation of  $\cdot\text{OH}$  in the process of FeOOH catalytic ozonation (without oxalic acid added) by means of ESR spin-trap technique, which can detect unstable radicals by measuring the intensity of DMPO- $\cdot\text{OH}$  adduct signal. The quantification of hydroxyl radicals is deemed to be possible at relatively low hydroxyl radicals production [33]. The spectra are recorded at intervals to monitor the evolution of the intensity of DMPO- $\cdot\text{OH}$  signal, and the results are summarized in Fig. 3. ESR spectra showed a typical four-line signal, having a peak height ratio of 1:2:2:1. The intensity of DMPO- $\cdot\text{OH}$  signals increased with the prolonging of recording time, which indicates that the DMPO- $\cdot\text{OH}$  adduct observed in this study are authentic. As shown in Fig. 3, the presence of FeOOH visibly increased the relative intensity of DMPO- $\cdot\text{OH}$  adduct signal. It can be inferred that the degradation of oxalic acid in FeOOH heterogeneous catalytic ozonation should be mainly attributed to hydroxyl radicals oxidation. Apparently, the ozone adsorption on FeOOH is the first and indispensable stage for its further decomposition into hydroxyl radicals. From Fig. 3, more hydroxyl radicals were produced at pH 7.0, while, it is found that the promoting effectiveness of FeOOH for hydroxyl radicals generation at pH 4.0 is more pronounced than that at pH 7.0. This should be due to the stronger self-decomposition of ozone into hydroxyl radicals at pH 7.0 than that of at pH 4.0 in homogeneous aqueous solution.



**Fig. 3.** Evolution of the relative intensity of DMPO- $\cdot\text{OH}$  adduct signal with and without FeOOH presence in ozonation system. Experimental conditions: ozone dose: 3.2 mg/L; FeOOH dose: 2 g/L; initial DMPO concentration: 100 mM;  $T = 293\text{ K}$ .

The surface hydroxyl groups have been proven to be the active sites for ozone decomposition and hydroxyl radicals generation in previous studies [9,34–36]; while, the neutral hydroxyl groups have been considered to be the active center promoting ozone decomposing, and it is believed that the  $\text{-OH}_2^+$  could weaken the nucleophilicity of the O of surface hydroxyl groups and decrease the interaction of the surface hydroxyl groups with ozone [9]. But from this experimental result, it indicates that the positive charge state of  $\text{Me-OH}_2^+$  also could effectively activate ozone to generate hydroxyl radicals. A newly published studying on ceramic honeycomb supported metals (Fe, Ni, and Zn) catalytic ozonation system also found the initiating ability of  $\text{-OH}_2^+$  on ozone decomposition and hydroxyl radicals production [36]. In fact, this is reasonable when considering the famous resonance structures of ozone molecule [37]. For its particular resonance structures, molecular ozone can react as a dipole, an electrophilic or nucleophilic agent. One of oxygen atoms with high electron density can display Lewis basicity, and then could react with the Brønsted acid  $\text{-OH}_2^+$ . The following reaction mechanism may be followed to explain the way of  $\text{-OH}_2^+$  to prompt ozone generating hydroxyl radicals (Eqs. (3)–(5), [36,38]). Likewise, ozone, behaving as Lewis base, can react with neutral state of  $\text{-OH}$  to generate hydroxyl radicals as shown in Eqs. (6)–(8) [11,38,39]. Furthermore, the hydroxyl radicals generated on the surface of catalyst will oxidize the oxalate ions adsorbed on the surface of FeOOH, or diffuse into the bulk solution to oxidize the nonadsorbed oxalic acid into carbon dioxide and water.



### 3.3. Effect of phosphate binding on the catalytic activity of FeOOH

#### 3.3.1. Phosphate adsorption on FeOOH

Phosphate has been observed to exhibit strong affinity on the surface of FeOOH [14,19,40]. Phosphate adsorption is thought to occur through ligand exchange accompanied by deprotonation of phosphate, and the replacement reactions possibly occurring at pH 4.0 and 7.0 are shown as below (Eqs. (9)–(18);  $\text{pK}_{\text{a}1} = 2.16$ ;



$pK_{a2} = 7.21$ ;  $pK_{a3} = 12.32$ ; [24,27,41]). Whether phosphate replaces one or two hydroxyls (i.e., forms a mononuclear or binuclear bond) on the surface is still a matter of debate [42]. The replacing of the surface hydroxyl groups is surmised to influence the adsorbing and catalyzing capacity of FeOOH.

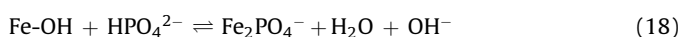
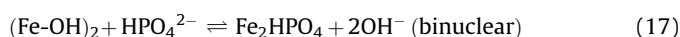
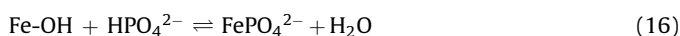
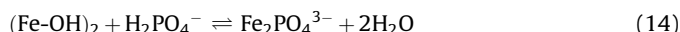
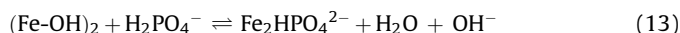
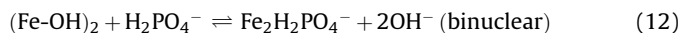
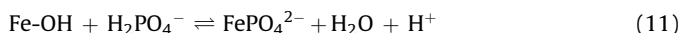
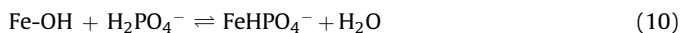
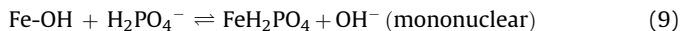


Fig. 4 shows the adsorption of phosphate on FeOOH. Phosphate is adsorbed onto goethite, and the extent of adsorption decreases with the increase of pH. It is known that the phosphate adsorption on FeOOH (see Eqs. (9)–(18)) depends on the pH of the solution as the contribution of  $\text{H}_2\text{O}$  and  $\text{OH}^-$  in ligand exchange is strongly pH dependant. At lower pH, the reactions presented in Eqs. (9)–(18) will easily take place [43], while, at higher pH, the ligand exchange reactions are weaker and even could be negligible due to the presence of  $\text{OH}^-$  ion, which is known to be the strongest monovalent Lewis base. It is worthy to be noted that the sulfate anion resulting from sulfuric acid for pH adjustment may interfere the adsorption efficiency of phosphate on FeOOH. The effect of sulfate on phosphate adsorption on FeOOH was checked in preparing test. Phosphate was reported to be a much stronger competitor than sulfate, and in systems with both of phosphate and sulfate anions, the influence of phosphate on sulfate adsorption was much stronger than vice versa, which reflects the higher affinity of phosphate for the goethite surface than sulfate [20]. As expected, the adsorption of phosphate on FeOOH was not affected in the presence of sulfate anion (data omitted here).

For its larger adsorption extent at lower pH condition, the FeOOHs used for phosphate adsorption experiments at pH 4.0 were filter out. The FeOOHs covered with different amount of phosphate

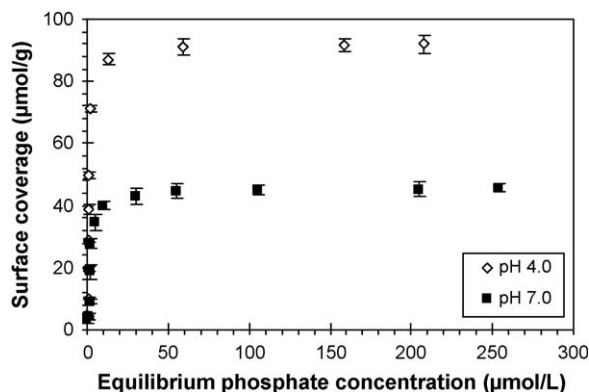


Fig. 4. Adsorption of phosphate on FeOOH. Conditions of experiments: FeOOH: 1 g/L;  $\text{NaNO}_3$ : 0.01 M;  $T = 293$  K.

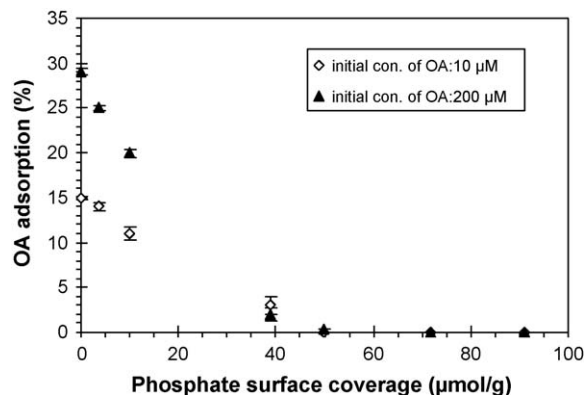


Fig. 5. Oxalic acid adsorption on phosphate bound FeOOH. Experimental conditions: FeOOH: 2 g/L (not include the weight of the binding phosphate); pH = 4.0;  $T = 293$  K.

were stored with Milli-Q water under pH 4.0 conditions for avoiding phosphate desorption. For the same reason, the experiments on the effect of phosphate binding on oxalate ions adsorption and its catalytic activity were carried out at pH 4.0 condition, too.

### 3.3.2. Adsorption of oxalate ions on phosphate bound FeOOH

As shown in Fig. 5, the adsorption efficiency of oxalate ions, with initial concentration of 10  $\mu\text{M}$  and 200  $\mu\text{M}$ , on phosphate bound FeOOHs both decreased with the increasing of the phosphate coverage, and no oxalate ions were adsorbed when the coverage of phosphate more than 49.8  $\mu\text{mol/g}$ . Furthermore, no phosphate desorption was detected in the presence of oxalate ions, even after continuously mixing for 48 h. It is obvious phosphate has stronger affinity than oxalate on FeOOH, and the deteriorative effect on oxalate ions adsorption seems to be nonreversible. The competitive adsorption of anions is affected directly by competition for surface sites and indirectly by the change of the electrostatic charge in the plane of adsorption [38].

### 3.3.3. Catalytic ozonation of oxalate ions in the presence of phosphate bound FeOOH

The experimental results of catalytic ozonation of oxalate ions in the presence of phosphate bound FeOOH are illustrated in Fig. 6. As anticipated, the binding of phosphate reduced the catalytic activity of FeOOH, and when the coverage is higher than 38.8  $\mu\text{mol}$  phosphate per gram of FeOOH, the negative impact became more evident (Fig. 6(a)). Phosphate is also the scavengers of hydroxyl

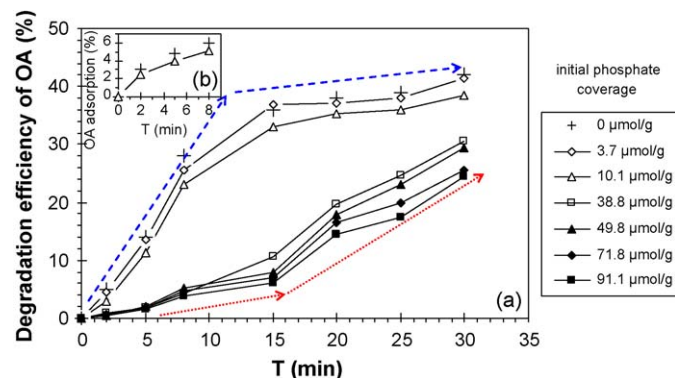


Fig. 6. Effect of phosphate binding on the catalytic activity of FeOOH (a) and the adsorption of oxalic acid (b). Experimental conditions: FeOOH: 2 g/L (not include the weight of the binding phosphate); initial concentration of oxalic acid: 0.01 mM; ozone gas flow rate: 400 mL/min; ozone gas concentration: 0.45 mg/min; pH = 4.0;  $T = 293$  K.

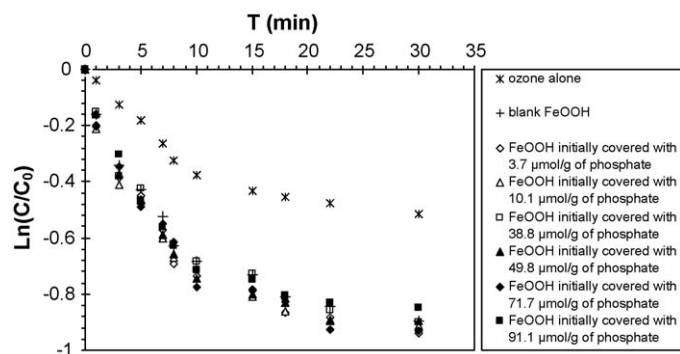
radicals [44]. At pH 4.0, the phosphate exists predominantly in the form of  $\text{H}_2\text{PO}_4^{2-}$  (99.4%, [27]), the competing consumption of hydroxyl radicals by  $\text{H}_2\text{PO}_4^{2-}$  with oxalate ions should be inferior due to the relatively low reaction rate constant with hydroxyl radicals ( $k_{\text{H}_2\text{PO}_4^{2-}}, \text{HO}^\bullet < 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , [44]). The deterioration of the catalytic activity may relate to the reduction of adsorption efficiency of oxalate ions on phosphate bound FeOOH, especially in the first 8 min that the effects of phosphate binding on oxalate ions adsorption and the catalytic activity of FeOOH followed the similar trend (Figs. 5 and 6). But, from Fig. 6, it is seen that corresponding to the abatement of 4.9% of degradation efficiencies of oxalate ions by catalytic ozonation processes with 10.1  $\mu\text{mol/g}$  phosphate bound FeOOH as catalyst in 8 min (Fig. 6(a)), only 0.9% of the reduction of adsorption efficiencies was observed (Fig. 6(b)), which further validates that the adsorption is not the critical reason for the catalytic activity of FeOOH on ozonation of oxalic acid.

Furthermore, from Fig. 6(a), the different influencing tendencies are observed with the different phosphate coverage corresponding to ozonation time. For FeOOHs with lower phosphate coverage (3.7 and 10.1  $\mu\text{mol/g}$ ), the degradation efficiency of oxalate ions presented the same trend with that of the blank FeOOH (no phosphate adsorbed). At the beginning of catalytic ozonation, the oxalate ions were degraded rapidly, and then followed with the platform degradation stage. But the degradation curves of oxalate ions appeared the concave inflexion in the ozonation processes catalyzed by the FeOOHs bound with more than 38.8  $\mu\text{mol/g}$  of phosphate coverage. In the first 8 min, it seems that these FeOOHs have lost their catalytic activity by comparing with the degradation efficiency of oxalate ions in ozonation alone systems (Fig. 1), while, in the following reaction time, the degradation efficiency of oxalate ions rapidly increases.

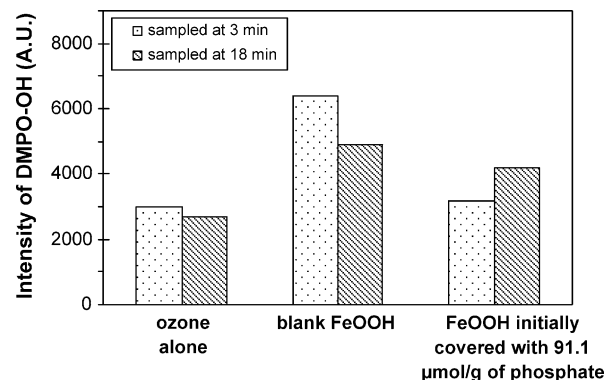
### 3.3.4. Ozone decomposition, hydroxyl radicals generation in the presence of phosphate bound FeOOH and the desorption of phosphate

Since both of the  $-\text{OH}_2^+$  and  $-\text{OH}$  are responsible for ozone decomposition on the surface of metal (hydr)oxides, theoretically speaking, the replacement of these groups by phosphate may hinder ozone decomposing into hydroxyl radicals, resulting in the deactivation of the catalyst.

Ozone decomposition in the presence of phosphate bound FeOOH is illustrated in Fig. 7. It is seen that the presence of FeOOH significantly promoted ozone decomposition. Though different initial surface coverage of phosphate on FeOOH led to distinct influencing trend on its catalytic activity, it had no influence on ozone decomposition. It is suspected that the generation of hydroxyl radicals should be different in the presence of blank FeOOH (without phosphate binding) and phosphate bound FeOOH. The samples for ESR determination were withdrawn at 3 min and



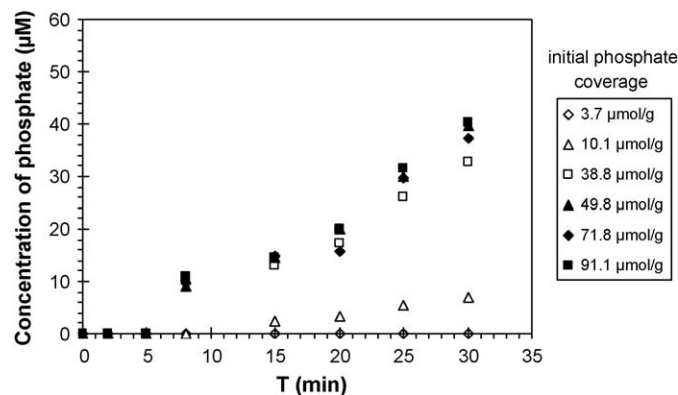
**Fig. 7.** Ozone decomposition in the presence of phosphate bound FeOOH. Experimental conditions: FeOOH: 2 g/L (not include the weight of the binding phosphate); initial concentration of ozone:  $13.7 \pm 0.2 \text{ mg/L}$ ; initial pH: 4.0; temperature: 293 K.



**Fig. 8.** Relative intensity of DMPO-OH adduct signal in ozone alone, blank FeOOH/ozone and phosphate bound FeOOH/ozone systems. Experimental conditions: ozone dose: 3.2 mg/L; FeOOH dose: 2 g/L (for phosphate bound FeOOH not include the weight of the binding phosphate); initial DMPO concentration: 100 mM;  $T = 293 \text{ K}$ .

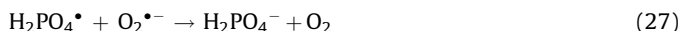
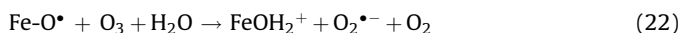
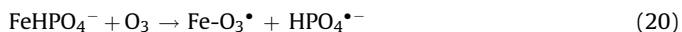
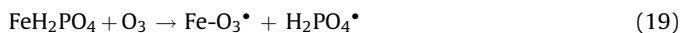
18 min, respectively. As illustrated in Fig. 8, it is obvious the phosphate binding on FeOOH hampered the generation of hydroxyl radicals. For the sample withdrawn at 3 min, the intensity of DMPO-OH signal decreased 23% in the presence of 91.1  $\mu\text{mol/g}$  phosphate bound FeOOH compared with that of the blank FeOOH, and the signal intensity was almost equal to that of in ozone alone system. The reduction of the generation of hydroxyl radicals should also be responsible for the degradation efficiency abatement in the phosphate bound FeOOH catalytic ozonation system in the first 8 min (Fig. 6). When sampled at 18 min, the intensity of DMPO-OH signal decreased in blank FeOOH/ozone system compared with that of at 3 min. However, for the FeOOH covered with 91.1  $\mu\text{mol/g}$  phosphate, the intensity of DMPO-OH signal increases 32% compared with that of at 3 min. For the blank FeOOH/ozone system, the falling of the DMPO-OH signal should be due to the gradual decrease of ozone concentration as shown in Fig. 7. While, for the phosphate bound FeOOH/ozone process, in which the concentration of ozone reduced similarly with that of in blank/ozone system, the boosting of the DMPO-OH signal for the sample withdrawn at 18 min is conjectured to be related to the regeneration of the catalytic activity of the phosphate bound FeOOH.

Since it is the phosphate binding that impairs the catalytic activity of the FeOOH, the phosphate in aqueous solution was measured. When exposed to the aqueous ozone, the phosphate was found to desorb from the surface of FeOOH (Fig. 9). It seems that ozone can make phosphate leaching from the surface of FeOOH. Since ozone can be treated as Lewis base due to its resonance structure, it is deduced that it is even harder than the



**Fig. 9.** Phosphate leaching exposed under ozone. Experimental conditions: FeOOH: 2 g/L (not include the weight of the binding phosphate); initial concentration of ozone:  $13.7 \pm 0.2 \text{ mg/L}$ ; initial pH: 4.0; temperature: 293 K.

surface bound phosphate, resulting in the leaching of phosphate from the FeOOH and the reactivating for the catalytic activity of FeOOH. Based on the experimental results, the possible reactions of phosphate leaching and the following way for hydroxyl radicals generation are postulated as shown below (Eqs. (19)–(27), [38,45–47]).



#### 4. Conclusions

The catalytic activity of FeOOH on ozonation of oxalic acid at pH 4.0 and 7.0 was studied. The FeOOH was found to effectively enhance the degradation efficiency of oxalic acid both at acidic and neutral pH conditions. Though adsorption of oxalate ions did part contribution for oxalate removal in FeOOH catalytic ozonation, but is not the critical reason for the catalytic activity of FeOOH on ozonation of oxalic acid. By means of ESR spin-trap technique, the presence of FeOOH was confirmed to promote the generation of hydroxyl radicals. It is deduced that the hydroxyl groups both of in neutral state (Me-OH) and positive charge state (Me-OH<sub>2</sub><sup>+</sup>) can perform as the active sites for ozone decomposition and hydroxyl radicals generation.

The ligand exchange of surface hydroxyl groups by phosphate deteriorated the adsorption of oxalate ions on FeOOH and the catalytic activity of FeOOH on ozonation. The deteriorative effect on oxalate ions adsorption should be nonreversible because no phosphate desorption was observed in the presence of oxalate ions. However, the phosphate was found to desorb from the surface of FeOOH in aqueous ozone solution, resulting in the reactivating of the catalytic activity of FeOOH. Since ozone, acting as the Lewis base, should be adsorbed and react with the hydroxyl groups on the surface of the catalyst, treated as Brønsted acid, it is deduced that whether the catalytic activity of the metal (hydr)oxides catalyst is affected depends on whether the coexisting Lewis bases are stronger or weaker than ozone.

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#### References

- [1] B. Kasprzyk-Hordern, M. Ziółtek, J. Nawrocki, *Appl. Catal. B: Environ.* 46 (2003) 639–669.
- [2] C.H. Wu, C.Y. Kuo, C.L. Chang, *J. Hazard. Mater.* 154 (2008) 748–755.
- [3] P.M. Álvarez, F.J. Beltrán, J.P. Pocostales, F.J. Masa, *Appl. Catal. B: Environ.* 72 (2007) 322–330.
- [4] M. Matheswaran, S. Balaji, S.J. Chung, I.S. Moon, *Catal. Commun.* 8 (2007) 1497–1501.
- [5] R.C. Martins, R.M. Quinta-Ferreira, *Appl. Catal. B: Environ.* 90 (2009) 268–277.
- [6] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Appl. Catal. B: Environ.* 79 (2008) 237–243.
- [7] C. Cooper, R. Burch, *Water Res.* 33 (1999) 3689–3694.
- [8] Z.Q. Liu, J. Ma, Y.H. Cui, B.P. Zhang, *Appl. Catal. B: Environ.* 92 (2009) 301–306.
- [9] T. Zhang, C.J. Li, J. Ma, H. Tian, Z.M. Qiang, *Appl. Catal. B: Environ.* 82 (2008) 131–137.
- [10] Y. Pi, M. Ernst, J.C. Schrotter, *Ozone Sci. Eng.* 25 (2003) 393–397.
- [11] M. Ernst, F. Lurot, J.C. Schrotter, *Appl. Catal. B: Environ.* 47 (2004) 15–25.
- [12] J. Randon, A. Larbot, L. Cot, M. Lindheimer, S. Partyka, *Langmuir* 7 (1991) 2654–2658.
- [13] L. Li, R. Stanforth, *J. Colloid Interface Sci.* 230 (2000) 12–21.
- [14] R. Rahnamaie, T. Hiemstra, W.H. Van, Riemsdijk, *J. Colloid Interface Sci.* 315 (2007) 415–425.
- [15] W.S. Yao, F.J. Millero, *Environ. Sci. Technol.* 30 (1996) 536–541.
- [16] T. Hiemstra, W.H. Van, Riemsdijk, *J. Colloid Interface Sci.* 225 (2000) 94–104.
- [17] T. Zhang, J. Ma, *J. Mol. Catal. A: Chem.* 279 (2008) 82–89.
- [18] J.S. Park, H. Choi, K.H. Ahn, J.W. Kang, *Ozone Sci. Eng.* 26 (2004) 141–151.
- [19] M.I. Tejedor-Tejedor, M.A. Anderson, *Langmuir* 6 (1990) 602–611.
- [20] J.S. Geelhoed, T. Hiemstra, W.H. Van Riemsdijk, *Geochim. Cosmochim. Acta* 61 (1997) 2389–2396.
- [21] J. Hoigné, H. Bader, *Water Res.* 17 (1983) 185–194.
- [22] T. Hiemstra, W.H. Van Riemsdijk, G.H. Bolt, *J. Colloid Interface Sci.* 133 (1989) 91–104.
- [23] L.P. Weng, L.K. Koopal, T. Hiemstra, J.C.L. Meeussen, W.H. Van Riemsdijk, *Geochim. Cosmochim. Acta* 69 (2005) 325–339.
- [24] W. Stumm, J.J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed., John Wiley & Sons, New York, 1996, pp. 533–541.
- [25] H. Bader, J. Hoigné, *Water Res.* 15 (1981) 449–456.
- [26] F.J. Beltrán, F.J. Rivas, L.A. Fernández, P.M. Álvarez, R. Montero-de-Espinosa, *Ind. Eng. Chem. Res.* 41 (2002) 6510–6517.
- [27] B. Legube, V.L.N. Karpel, *Catal. Today* 53 (1999) 61–72.
- [28] R.D. Lide, *CRC Handbook of Chemistry and Physics*, 87th ed., CRC, Taylor and Francis, Boca Raton, FL, 2007, pp. 8–42.
- [29] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Refer. Data* 17 (1988) 513–886.
- [30] J. Staehelin, J. Hoigné, *Environ. Sci. Technol.* 16 (1982) 676–681.
- [31] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, *Appl. Catal. B: Environ.* 47 (2004) 101–109.
- [32] J. Ma, M.H. Sui, T. Zhang, C.Y. Guan, *Water Res.* 39 (2005) 779–786.
- [33] S.K. Han, S.N. Nam, J.W. Kang, *Water Sci. Technol.* 46 (2002) 7–12.
- [34] L. Zhao, Z.Z. Sun, J. Ma, H.L. Liu, *Environ. Sci. Technol.* 43 (2009) 2047–2053.
- [35] L. Yang, C. Hu, Y.L. Nie, J.H. Qu, *Environ. Sci. Technol.* 43 (2009) 2525–2529.
- [36] L. Zhao, Z.Z. Sun, J. Ma, *Environ. Sci. Technol.* 43 (2009) 4157–4163.
- [37] W.D. Bellamy, F. Domez, B. Langlais, A. Montiel, K.L. Rakness, D.A. Reckhow, C.M. Robson, in: B. Langlais, D.A. Reckhow, D.R. Brink (Eds.), *Ozone in Water Treatment: Application and Engineering*, Lewis Publishers, Chelsea, MI, 1991, pp. 317–468.
- [38] R.E. Buhler, J. Staehelin, J. Hoigné, *J. Phys. Chem.* 88 (1984) 2560–2564.
- [39] L. Zhao, Z.Z. Sun, J. Ma, H.L. Liu, *Appl. Catal. B: Environ.* 89 (2009) 326–334.
- [40] J.S. Geelhoed, T. Hiemstra, W.H. Van Riemsdijk, *Environ. Sci. Technol.* 32 (1998) 2119–2123.
- [41] N. Nilsson, L. Lovgren, S. Sjöberg, *Chem. Spec. Bioavailab.* 4 (1992) 121–130.
- [42] P. Persson, N. Nilsson, S. Sjöberg, *J. Colloid Interface Sci.* 177 (1996) 263–275.
- [43] J. Nawrocki, M.P. Rigney, A. McCormick, P.W. Carr, *J. Chromatogr. A* 657 (1993) 229–282.
- [44] W.J. Masschelein, *Unit Processes in Drinking Water Treatment*, Marcel Dekker, New York, 1992, pp. 67–122.
- [45] J. Staehelin, R.E. Buhler, J. Hoigné, *J. Phys. Chem.* 88 (1984) 5999–6004.
- [46] H. Tomiyasu, H. Fukutomi, G. Gordon, *Inorg. Chem.* 24 (1985) 2962–2966.
- [47] P. Maruthamuthu, P. Neta, *J. Phys. Chem.* 82 (1978) 710–713.